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**A RELIABLE, MAINTENANCE-FREE OXYGEN SENSOR FOR
AIRCRAFT USING AN OXYGEN-SENSITIVE COATING ON
POTENTIOMETRIC ELECTRODES**

Emory S. De Castro, Ph.D.

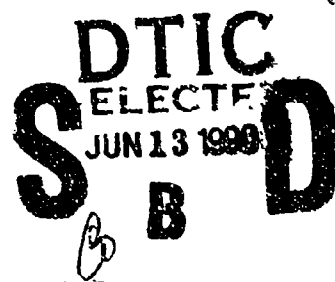
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Brooks Air Force Base, TX 78235-5301



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NOTICES


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The Office of Public Affairs has reviewed this report, and it is releasable to the National Technical Information Service, where it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for publication.


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<p>This report is on the preliminary development of a new kind of oxygen sensor. Based on sensing a potentiometric signal from oxygen-specific compounds, this approach offers a potentially stable, reliable, and vastly simplified sensor. The report represents two configurations for the oxygen-specific compound (oxygen reagent). One makes use of the reagent in a thin solution film confined by a membrane. The other uses the reagent immobilized in a polymer film, without any additional solvents. This last embodiment is essentially a solid-state probe for oxygen. This report demonstrates the feasibility of such an approach by reviewing relevant work dealing with 1) proof of principle, 2) calibration curves over a range of oxygen pressure, 3) temperature effects, and 4) pressure effects.</p>					
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A RELIABLE, MAINTENANCE-FREE OXYGEN SENSOR
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INTRODUCTION

On-Board Oxygen Generation Systems (OBOGS) require a reliable maintenance-free oxygen sensor. Traditional approaches make use of either amperometric or galvanic sensing techniques. Oxygen is consumed in both. The current produced is related to oxygen concentration. Both of these techniques are inherently unstable because oxygen reduction products (ultimately) destroy the sensor. A passive oxygen sensor could circumvent these limitations.

A potentiometric sensor uses passive oxygen recognition. The oxygen participates in an equilibrium with an oxygen-specific reagent. The ratio of oxygen-bound to oxygen-free reagent is sensed as a potential versus a reference electrode. Since oxygen is not being consumed, oxygen degradation products do not poison the sensor. Additionally, the reagent can be incorporated into a polymer film, eliminating the traditional solution electrolyte. This design is analogous to the solid-state pH electrode. By employing a solid-state film, extreme conditions like rapid depressurization should not affect probe stability (i.e., one cannot have bubbles occluding the electrode). An ideal oxygen sensor should result from combining an oxygen-sensitive film with a potentiometric electrode.

Much of this contract's work details the feasibility of designing a solid-state oxygen sensor, i.e., a potentiometric oxygen-sensing probe which will incorporate an oxygen-sensitive polymer film. In order for the system to be well-characterized, most of the work was performed using thin solution films of the reagent. However, we also demonstrated solid-state sensors made from oxygen-sensitive polymer films.

Work for this contract includes derivation of theoretical response functions for both mono- and bi-nuclear oxygen reagents. Theory is compared to experimental results. We identified parameters which control the range of sensor response, and parameters which affect the sensor response. Key results are:

1. Proof of Principle: Figure 1 demonstrates a reversible potentiometric response for an oxygen reagent. Figure 2 demonstrates a reversible potentiometric response for an oxygen reagent in a thin polymer film. These are cycled between 0 and 100% oxygen.
2. Calibration: Figures 3 and 4 are different probes' responses to systematic changes in oxygen concentration. Figure 3 shows response of a prototype probe immersed in oxygen/nitrogen gas mixtures. Figure 4 shows response of a solid-state example of a reagent in a polymer film. The experimental section of the text details how the reagent's oxygen affinity controls the probe's response range.
3. Temperature: Figure 5 is the result of a thin solution film probe's temperature response. A slope of roughly 1-3% of full scale voltage per degree K is obtained.
4. Pressure: A severe evacuation or pressurization of the gas sample results in the response shown in Figure 6. The probes appear stable to a few mV of original response. (Note extreme vertical exaggeration used; change in signal is <1%.) (Reagent in a thin solution film.)



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5. Solid-State: Figures 2, 4, and 11 confirm that a thin polymer film can be incorporated into a potentiometric sensor.

These 5 items specifically address the needs of an oxygen sensor in an OBOGS. Figures 2, 4, and 11 indicate the potentiometric sensor, as envisioned with polymer film, has potential for use in an OBOGS. The following sections describe in more detail other relevant areas such as probe longevity, parameters which control sensor response, the theoretical response function, and oxygen sensitive films.

STABILITY ASPECTS

Longevity

The focus of this program is to provide proof of principle, establish feasibility, and indicate the likelihood of being able to produce a stable sensor. Sensor stability is threatened by external and internal problem areas. External influences for probe breakdown could be extremes in temperature, pressure, and humidity. Internal problems involve reagent and reference-electrode stability.

A potentiometric approach moves the likely probe failure mechanism from the chemistry of oxygen reduction to the chemistry of oxygen reagents. We have shown more than 6 days of stable, continuous use for a solution-type sensor (Figure 7). Similarly, the oxygen-sensitive films appear to last for at least 10 days (interim report to Aqualytics, University of Michigan, 4/89).

Temperature/Pressure

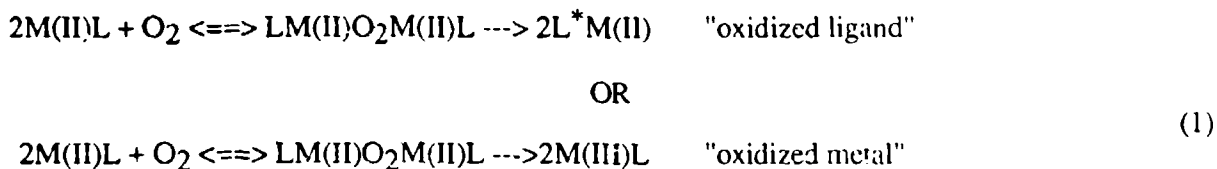
One envisioned advantage of the polymer film would be its resistance to both pressure and temperature changes. Elimination of the electrolyte reduces the possibility of bubbles, freezing, boiling, or low humidity posing a measurement problem.

Figures 5 and 6 show temperature and pressure effects. In Figure 5, we measured oxygen concentration in an iso-thermal water bath. The probe's response is corrected by subtracting the percent decrease in actual oxygen content from the probe response. A linear fit to this corrected response yields a change of 1.5 ± 0.6 mV/°K. Given a full scale response of 50-100 mV, this represents 3-6%/°K. No temperature dependence studies were performed on the solid polymer films.

To obtain data for Figure 6, the sensor was placed in a gas-tight chamber, and allowed to achieve a steady-state response in air. The chamber was then subjected to either vacuum (5 in. Hg) or pressurized air (40 psi). The probe shows remarkable stability in the face of such massive pressure changes ($<1\%$ full scale for $\Delta P \geq 40$ psi).

Chemical Degradation of Sensor

There are two general pathways to degrade an oxygen reagent; one is reversible, the other is permanent:



Ligand oxidation is irreversible. Metal oxidation can be considered reversible. Figures 8a through d show the results from a series of experiments to demonstrate these pathways.

Figure 8a is the UV-VIS spectrum of a solution of fresh reagent (#72). The absorption at 300 nm is due to the reagent's metal-oxygen charge transfer band. By electrochemically oxidizing this solution, the band disappears and one concludes there is no oxygen binding to the metal (III) complex. Further electrochemical reduction restores the metal-oxygen charge transfer band. Figure 8b results from using a 30-day-old solution of reagent #72, which has been chemically oxidized. It shows no metal-ligand charge transfer band, and electrochemical reduction does not restore the metal-oxygen charge transfer band. This reagent would be considered "ligand oxidized".

In Figure 8c, a fresh solution of reagent #190 displays the familiar metal-oxygen charge transfer band. Electrochemical cycling is possible between oxidized and reduced states. This cycling identifies the metal-ligand charge transfer band as well as providing a spectrum of the metal (III) form. After 60 days exposure to air, we obtained an "oxidized" spectrum (Fig. 8d). Electrochemical reduction shows regeneration of oxygen-binding capacity for the reagent. In short, this has rejuvenated the sensor reagent.

Aquanaautics currently funds a synthetic chemistry program at the University of California, Davis, headed by Professor Kevin M. Smith and staffed by an Aquanaautics Senior Scientist, three postdoctoral assistants, and a research assistant. This group has produced more than 200 oxygen-binding compounds. In 1989, the focus for this group shifted to synthesizing compounds especially resistant to ligand and metal oxidation (i.e., which are highly stable).

Figure 9 shows some achieved stabilities. (Spectroscopic half-life is measured by recording the intensity of the metal-oxygen charge transfer band over time.) Figure 9 represents 2 classes of oxygen reagents which have systematic changes in ligand structure. Note how small structural changes can dramatically influence compound stability.

The literature reports enhanced stabilities for oxygen-binding compounds that have been immobilized in a polymer network.^{1,2,3} The researchers claim immobilization inhibits dimer formation. The dimer is believed to be the necessary precursor to oxidative degradation. We anticipate our reagents will have enhanced stabilities when immobilized on/in polymers. Currently, reagents in polyvinyl chloride films appear stable for at least 10 days.

Because the potentiometric sensor is composed of a sensing electrode and a reference electrode, the reference electrode must be considered as well. The stability of an electrochemical reference electrode depends on two factors. One is the stability of the chemical equilibrium governing the reference potential. Our systems employ the Ag/AgCl electrode because the $Ag^0 + Cl^- \rightleftharpoons AgCl$ equilibrium is well characterized. For this equilibrium to remain unchanged, very little current should flow between the sensing and reference electrodes. The second contribution to instability is current flow through the reference electrode. One of the stability problems in the traditional polarographic/galvanic oxygen sensors is current flow during oxygen consumption (reduction). This current can ultimately change the composition of the Ag/AgCl reference, as well as the nature of the working electrode.⁴ In any potentiometric

approach, one uses as small a current as possible to make the voltage measurement between sensing and reference electrode (higher resistance in the measurement loop = lower current). The needed high resistances are analogous to the high impedances of a pH electrode. The oxygen-sensitive polymer films are very much like a pH electrode in that they provide very high impedance. The resulting small measurement currents lead to a more stable, maintenance-free reference electrode.

Because this work focused on selective oxygen sensing, very little effort was spent on investigating the reference electrode. However, we did find that electroplating Cl^- onto the reference electrode substantially improved probe stability and response.

THEORY: PARAMETERS AFFECTING PROBE RESPONSE

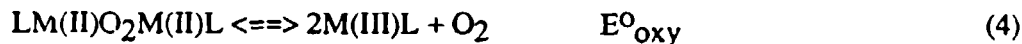
The basis for a potentiometric measurement comes from Nernst's mathematical description of an electrode in an ionic solution, which relates solution potential to the ratio of oxidized and reduced species:

$$E = E^0 + (RT/nF)\ln[\text{ox/red}] \quad (2)$$

wherein: E is the solution potential, E^0 = formal reduction potential, R = gas constant, T = temperature in $^{\circ}\text{K}$, n = electron stoichiometry upon changing redox state, F = Faraday's constant, and $[\text{ox/red}]$ = ratio of oxidized to reduced concentrations.

Conceptually, one can envision the electrode as an intermediate in an electron cross reaction. For example, a solution of metal (II) and metal (III) is capable of transferring electrons from one molecule to another. As long as an oxidation occurs with a reduction, there is no net change in solution potential. If a piece of metal is added to the solution, and this metal's potential is different from that of the solution, then its potential will change to meet the solution potential. That is, if the metal's potential is more positive (+) than the solution's, the electrode will accept "excess" negative charge from the metal (II), until its potential is the same as the solution. Hence, the electrode "tracks" solution potential.

Our sensor operates on this same principle. We begin with a description of possible reagent species.



Three Nernstian species exist: M(II)L (reduced deoxy), $\text{LM(II)O}_2\text{M(II)L}$ (reduced, oxygen bound), and M(III)L (oxidized). M(III)L is common to both Eqs. 3 and 4. A single relation describing the overall solution potential is the oxygenation reaction (from Eqs. 3 and 4):



Similarly, the Nernst Equation can be reformulated using equations 3, 4, and 5:

$$E_{\text{sensed}} = E^0 + (RT/2F)\ln[(\text{LM(II)O}_2\text{M(II)L})/(\text{M(II)L})^2(\text{O}_2)] \quad (6)$$

Equation 6 can be expanded and rewritten to reflect the conditions under which we employ an oxygen reagent. Eq. A-8 in the Appendix concludes with the response function of the probe.

Both Appendix Eq. A-8 and Eq. 6 above show that the sensed potential is a function of the ratio of bound to free reagent, reagent concentration, oxygen affinity of the complex, and oxygen concentration.

A reagent immobilized in a polymer film should result in a monomeric oxygen reagent. Thus,



and substituting into Nernst's Equation (Equation 2),

$$E_{sensed} = E^0 + (RT/F) \ln 1/K_{O_2}[O_2] \quad (8)$$

where K_{O_2} refers to the overall binding affinity. Because of a much simpler stoichiometry, the Nernst formulation shows a response function that is independent of reagent concentration and has a steeper response slope. A polymer film carrier is anticipated to yield a slope of 59 mV/decade of oxygen concentration at 25°C. In contrast, the solution example predicts 28.5 mV/decade (at 25°C). More detailed calculations are included in the appendix, as well as some simulations linking full-scale probe response to the oxygen binding constant for the solution case.

Response slope is generally greater for polymer-confined reagents than for solution reagents (60+ mV/decade vs. 25-40 mV/decade) (Figs. 3 and 4).

EXPERIMENTAL: PARAMETERS AFFECTING PROBE RESPONSE

Both derivations indicate probe response is dependent on oxygen affinity, but a reagent with very high affinity is not necessarily best. High affinity reagents can chelate the analyte too well, hence fail to release bound oxygen, or do so very slowly. A nonreversible sensor would be the outcome. Thus, the initial phase involved evaluation of some potential oxygen reagents (Table 1). Reagents were screened by following the potentiometric response resulting from a thin solution layer of reagent being subjected to cycles of inert gas or 1 ATM oxygen. Those reagents having a suitably stable signal were then further tested (Table 1, reagents 150 and 189).

Overall oxygen affinity is an important factor in selecting a reagent because as the oxygen affinity is lowered, the quantity of oxygen needed to saturate the reagent is increased. These two reagents serve as good examples of the link of response to oxygen affinity (Eq. 5; Appendix Eq. A-8). Oxygen affinity for #189 is $\text{Log } K_{O_2} = 7.8$. This reagent is sensitive to the lower % oxygen regions, i.e., up to about 20% O_2 (Fig. 10). By comparison, reagent #150 has $\text{Log } K_{O_2} = 6.7$, and its response range extends to 80% oxygen before reagent saturation (Fig. 3). For a confident 100% oxygen response, one needs either a slightly lower affinity reagent or a good mathematical description of the data. Thus, overall oxygen affinity is an important factor in selecting a reagent.

The calibration plots for reagent #150 are given for two different probes. For each case, a least squares fit is used to derive either a linear or second order polynomial fit. As anticipated by Eq. 6 or Eq. A-8, the polynomial fit has a better correlation to experimental data. For example, linear (least-squared) fits to the data (Figs. 3A and 3B, top graphs) yield correlation coefficients of 0.808 and 0.881. The second order polynomial fit (also least squared) yields correlation coefficients of 0.985 and 0.992.

TABLE 1. SCREENING OF OXYGEN REAGENTS

The following were cycled between 100% oxygen or argon. Cycles varied between 10 and 30 min. All signals were recorded from the gas phase. All reagents were in a thin layer of solution.

Reagent	Cycle	% decline (at last cycle)
64	1	not reversible
78	26	30
85	3	95
90	17	75
91	17	95
118	35	80
142	3	95
147	31	"stable"
150	25	15
161	42	"stable"
164	16	80
166	12	50
189	38	"stable"

The Nemst equations describing probe response contain a temperature-related slope, RT/nF : one would expect a change of $0.2 \text{ mV}/^\circ\text{K}$. Because we have obtained slopes of $1.5 \pm 0.6 \text{ mV}/^\circ\text{K}$, other contributions to probe response must exist. The Ag/AgCl reference potential is temperature dependent. The overall reagent oxygen affinity is also temperature dependent. As temperature increases, oxygen affinity decreases. Nevertheless, all these factors appear to combine in a linear fashion (Fig. 5). A linear temperature profile means a simple electronic circuit can compensate for temperature drift, making probe design, construction, and calibration simpler.

We investigated a probe's response profile over a range of solution compositions; we changed pH, ionic strength, and ionic composition. Probe behavior follows the predicted response: when the sensor reagent is prepared in a solution which inhibits oxygen binding (high ionic strength, low pH, or containing oxy-anions); then the probe response requires greater oxygen concentrations before saturation. For example, at $\text{pH}=8$, reagent #150 exhibits 90% of full scale response in a 50% (v/v) oxygen environment. At $\text{pH } 7$ (low oxygen affinity), the 50% response signal moves to 50% of full scale.

OXYGEN-SENSITIVE POLYMER FILMS: TOWARDS A SOLID-STATE OXYGEN SENSOR

There are several advantages to combining the above potentiometric response with an oxygen reagent immobilized in a polymer film: bubble formation is eliminated, and maintenance of probe integrity in low humidity environments should not be a problem. Since an immobilized reagent is most likely a monomer, the response function dramatically simplifies to Eqs. 7 and 8, probe response is no longer a complicated function of reagent concentration. A monomer should have a more linear calibration plot than a dimer. A predicted slope of 60 mV/decade oxygen concentration indicates monomers should have a greater sensitivity to oxygen. Researchers have reported compounds similar to ours being more stable upon immobilization (1-3). We anticipate being able to construct a long-lived and stable probe built upon polymer films.

This report demonstrates proof-of-principle for such a solid-state oxygen sensor. The following figures present results obtained by sampling oxygen in solution. The simple probe is constructed of only working and reference electrodes and the polymer film; it uses no other fluids. Figure 2 shows data from a high-affinity reagent immobilized in a thin film of polyvinyl chloride. The probe generated a change of nearly 250 mV upon cycling from nitrogen to air. Calibration yielded a very linear (correlation coefficient = 0.992) plot over a low O_2 range ($0.6 \rightarrow 7.0\%$), but beyond 10% oxygen the reagent is saturated (Fig. 4). "Polymer" linearity is better than for the "reagent in solution" (e.g., Fig. 3 has a correlation coefficient = 0.93). Better linearity of the polymer-immobilized case agrees with theory.

The solid-state probe also shows a shifting of a reagent's saturation zone when overall oxygen affinity is lowered. Figs. 10 and 11 compare calibration plots for reagent #189 in a thin solution phase versus in a thin polymer film. Immobilization in the film decreases the reagent's oxygen affinity. Thus, the effective upper range changes from 0.2 ATM oxygen in solution to 0.5 ATM oxygen in the polymer film. Similarly, upon comparing the moderate affinity #189 (in polymer film, Fig. 11) to high-affinity #33 (also in polymer film, Fig. 4) we noted a shift in "high end" from 0.08 ATM oxygen to 0.5 ATM oxygen. Furthermore, the slopes of solid-state response plots are 60 mV/decade or greater, while solution reagents are around 30 mV/decade . These slopes are in accordance with that predicted by Eqs. A-8 and 8 for dimeric and monomeric reagents.

These films are expected to be stable. Reagent #33 has given reproducible results for at least 10 days in a thin polymer film. Experiments monitoring longer-term stability are the subject of a Phase II proposal.

SUMMARY

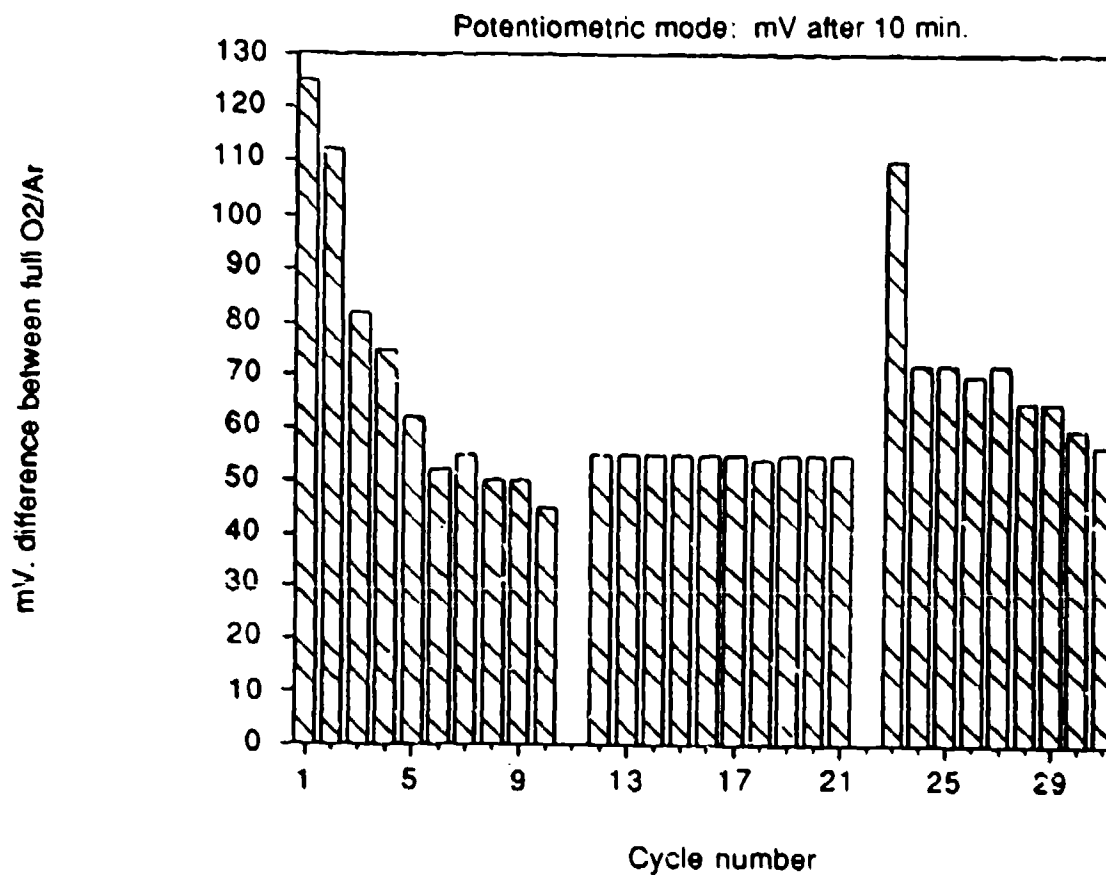
This work demonstrates a solid-state oxygen-sensing device, and, we confirmed conditions which control the sensor's response range. Preliminary tests indicate the potentiometric approach is feasible for operation under OBOGS conditions. Presently unknown, and the subject of a phase II proposal, is the long-term stability of such a sensor.

ACKNOWLEDGEMENTS

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REFERENCES

1. Wang, J.H., Hemoglobin Studies. II. A synthetic material with Hemoglobin-like property, JACS, 58, Part 2:3168-3169, 1958.
2. Jones, R.D., D.A. Summerfield, and F. Bassolo, Synthetic oxygen carriers related to biological systems, Chem Reviews, 79:139-179, 1979.
3. Shiegehara, K., et. al., Macromolecules, 14:1153, 1981.
4. Lucisano, J.Y., J.C. Armour, and D.A. Gough, In vitro stability of an oxygen sensor, Analytical Chemistry, 59:736-739, 1981.



- Note: 1) Cycle 11 is probe in air 16 hours
2) Cycle 22 is probe in N₂, 1 hour

Figure 1. Reagent #147: 1ATM O₂/Ar.

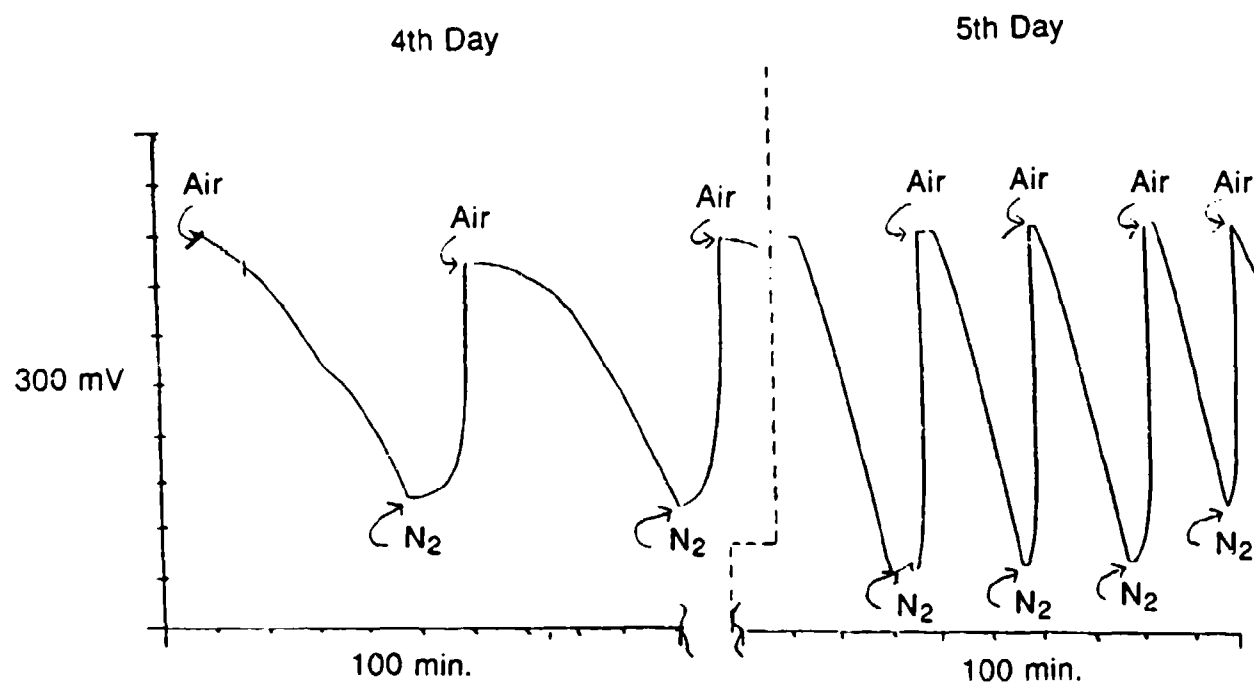


Figure 2. Raw data of reagent #33 in PVC film, cycle between N₂ and air. Fourth and fifth day of testing.

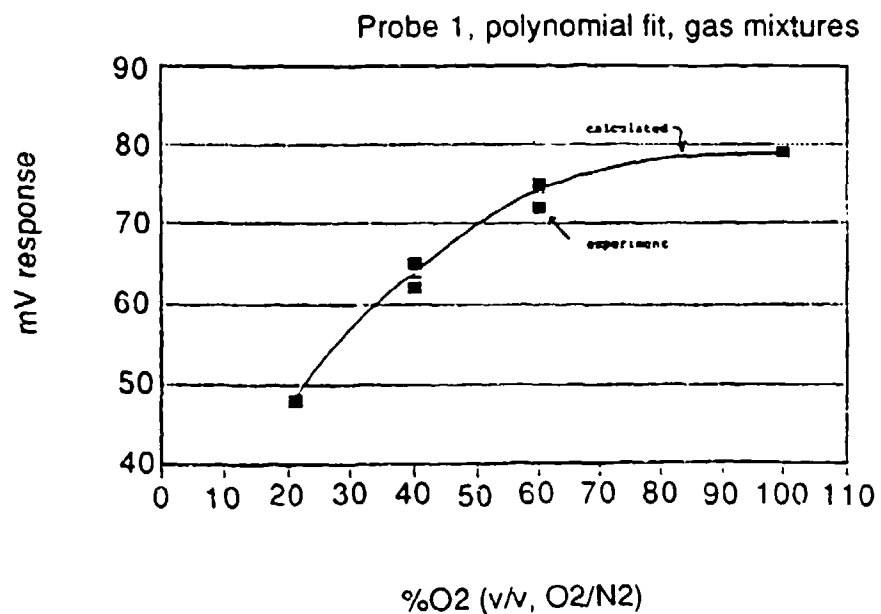
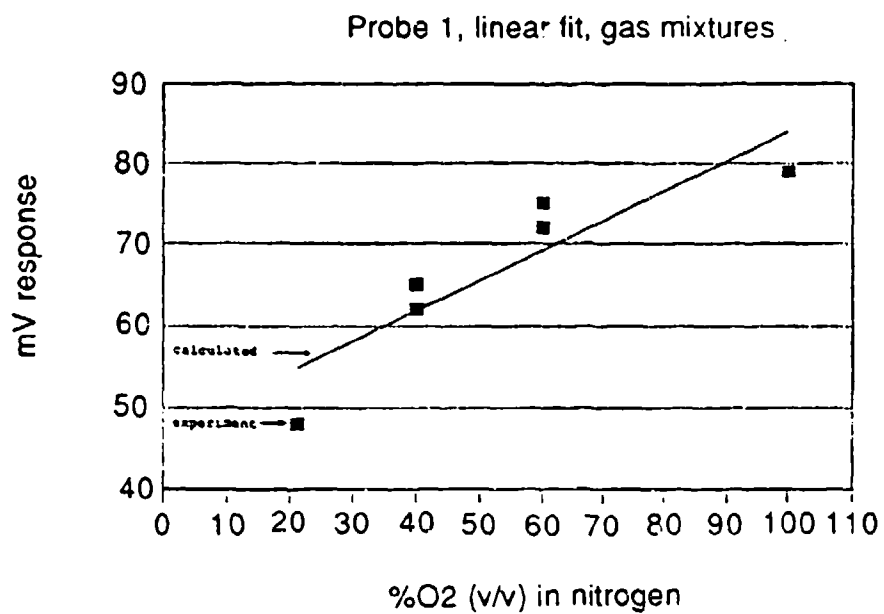


Figure 3A. Probe calibration: Reagent #150.

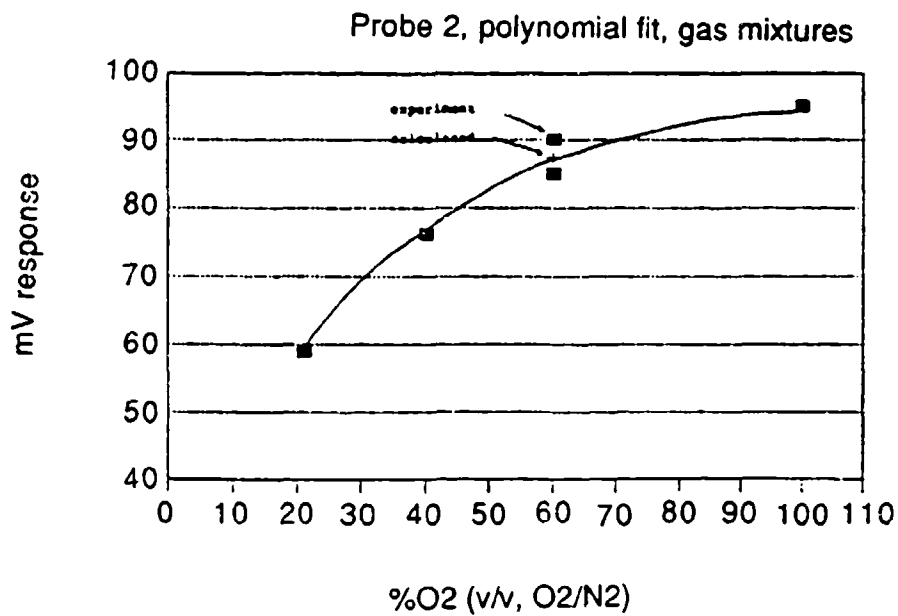
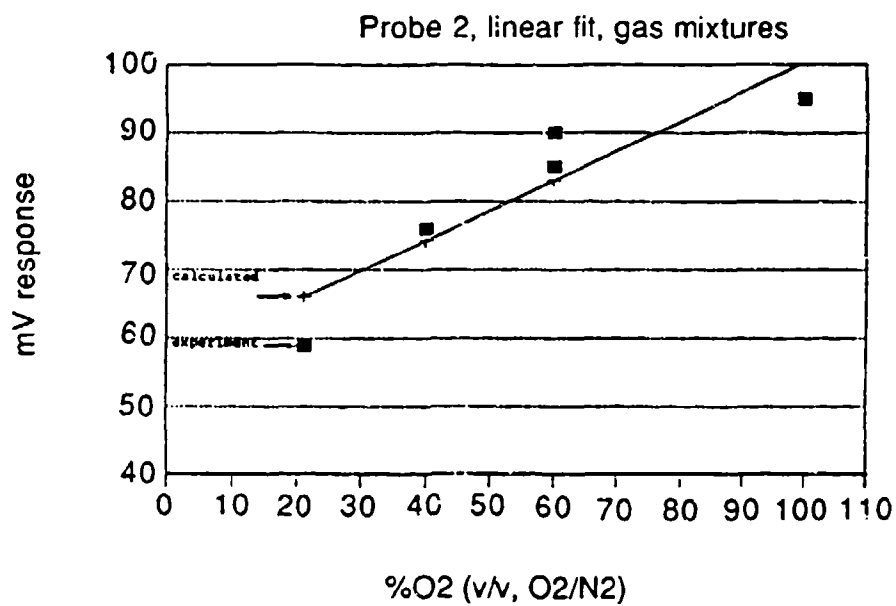
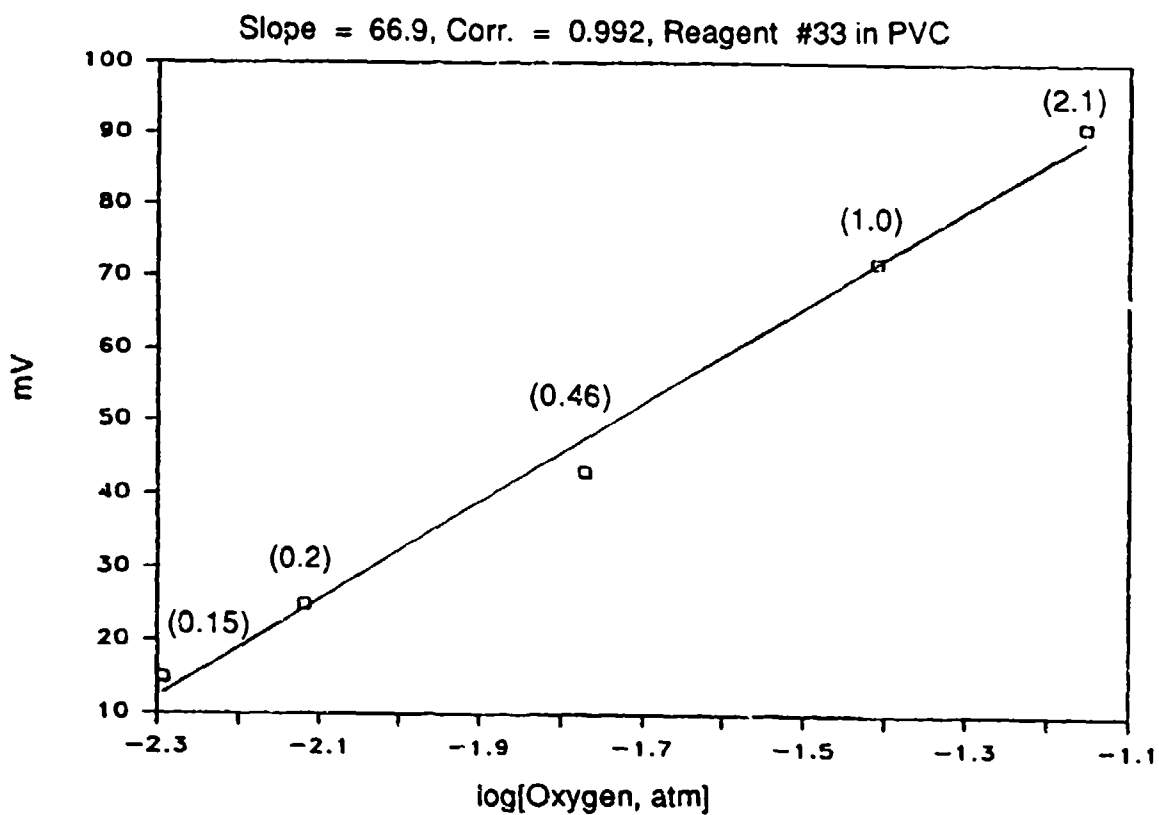


Figure 3B. Probe calibration: Reagent #150.



Note: Numbers in parenthesis are ppt (mL O₂/L H₂O)

Figure 4. Calibration curve of oxygen sensor.

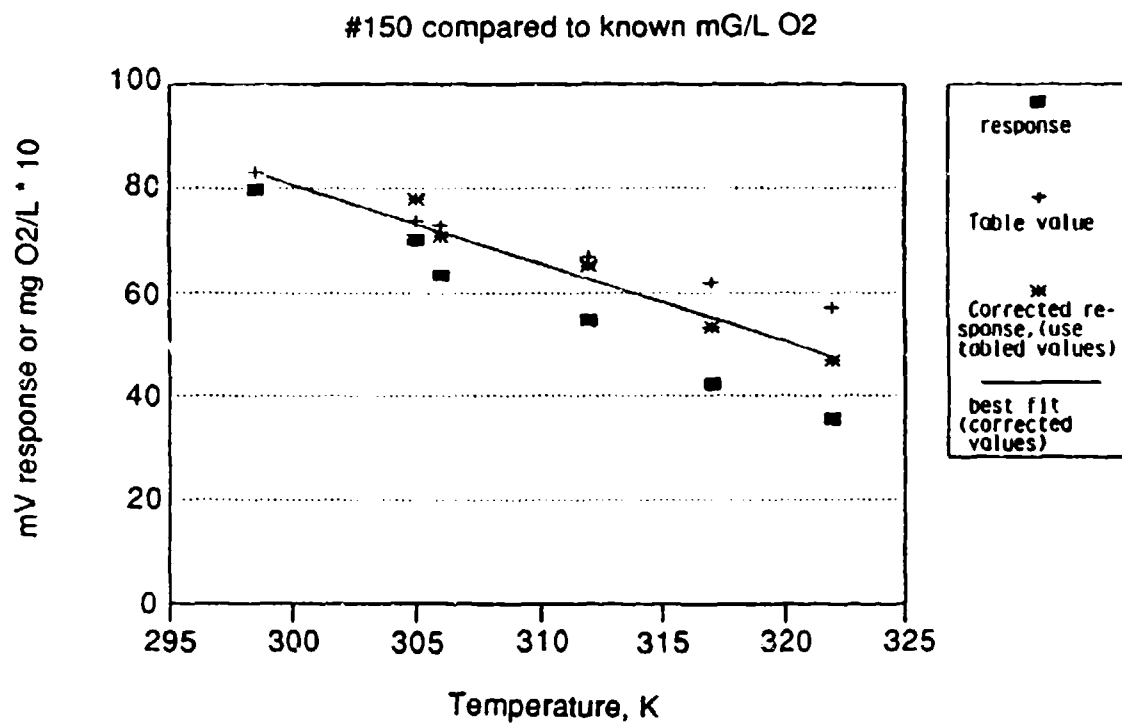


Figure 5. Probe response vs. temperature.

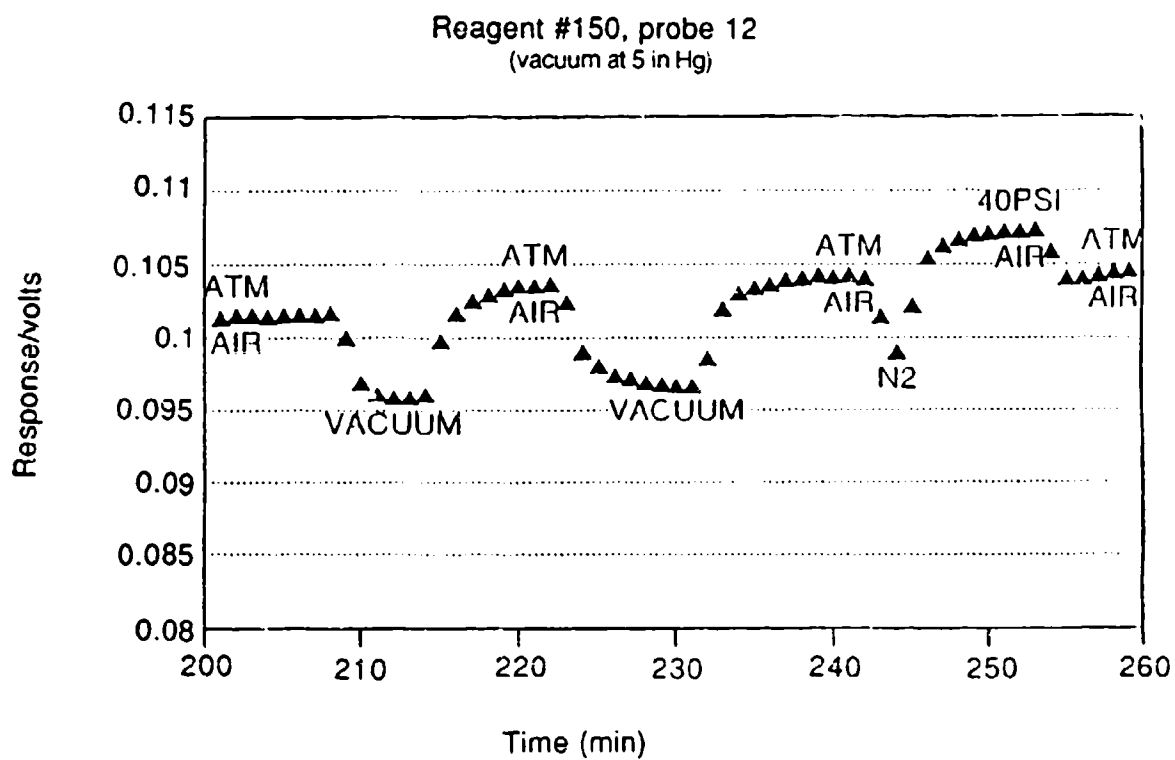


Figure 6. Sensor under pressure change.

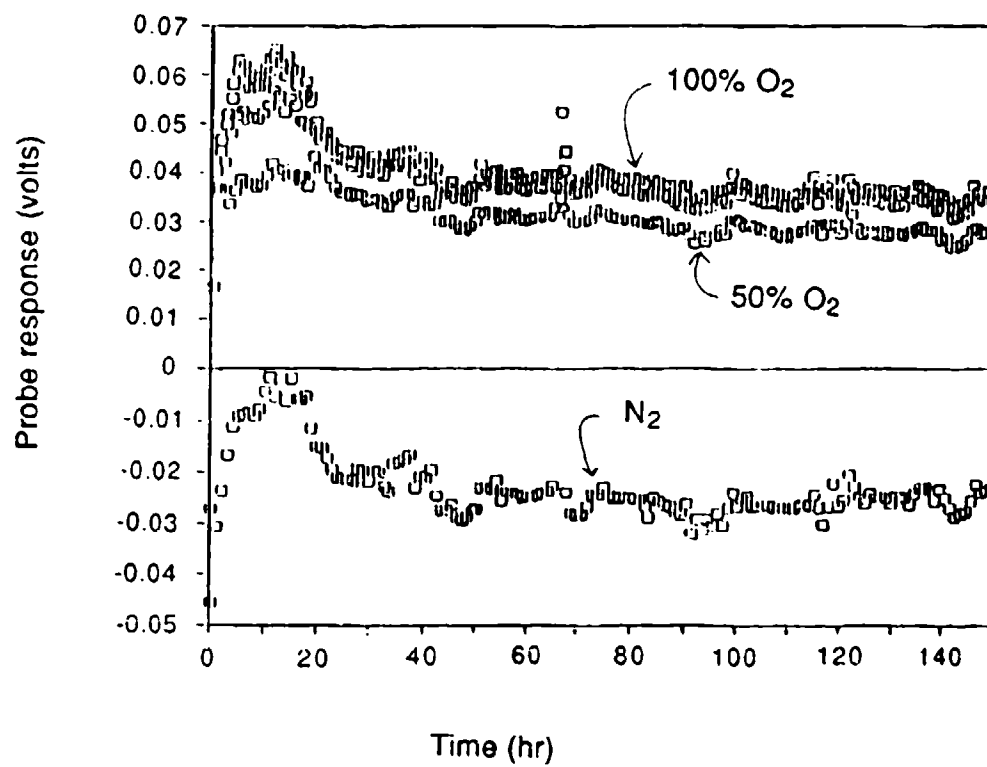
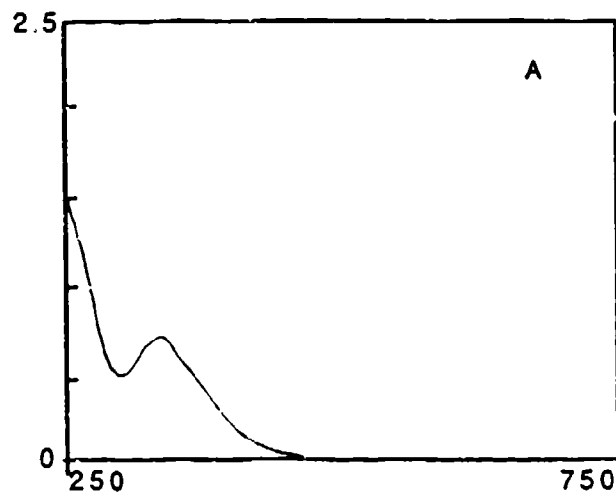
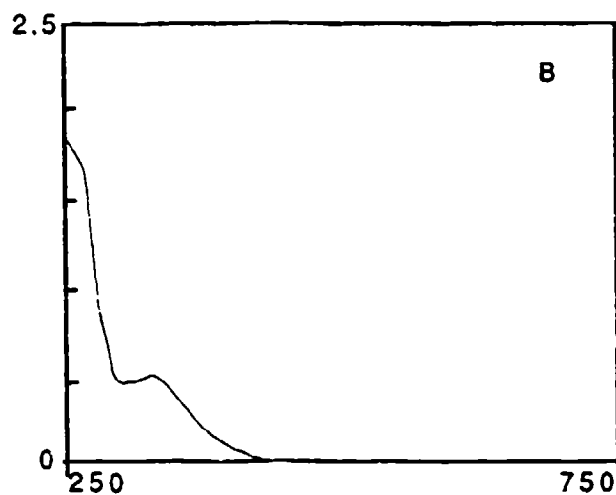


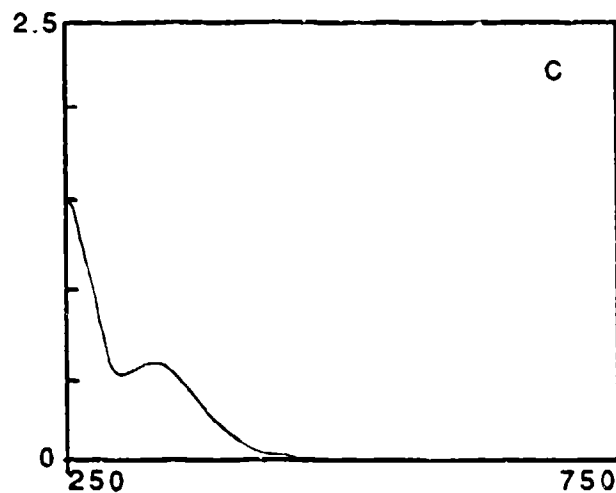
Figure 7. Life time study of #189.



FRESH
Open Circuit
Quartz/Carbon OTTE
4 mM Reagent, pH=7, 0.1 M KCl



OXIDIZED
As above, after 25 min. at
0.8 V vs. Ag/AgCl



REDUCED
As above, after 25 min.
at -0.25 V vs. Ag/AgCl

Figure 8a. Ligand vs. metal oxidation for reagent
Case: ligand oxidized
Reagent 72, fresh

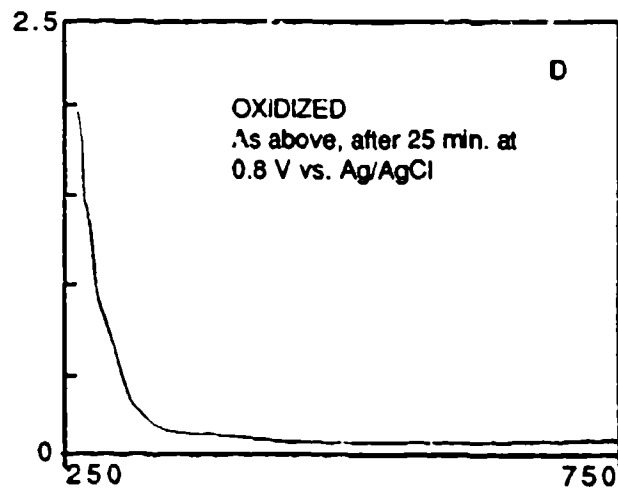
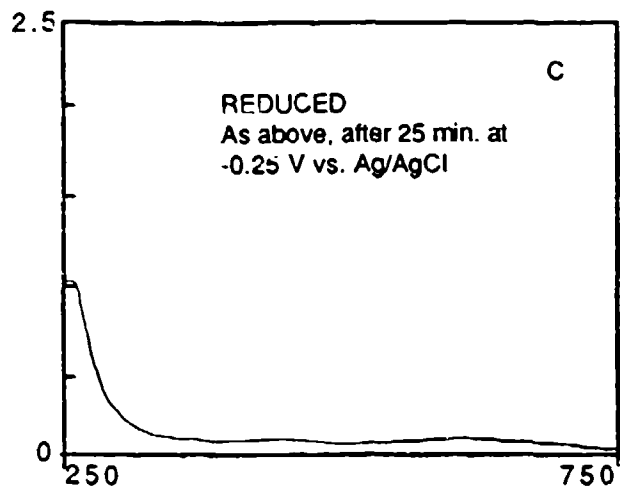
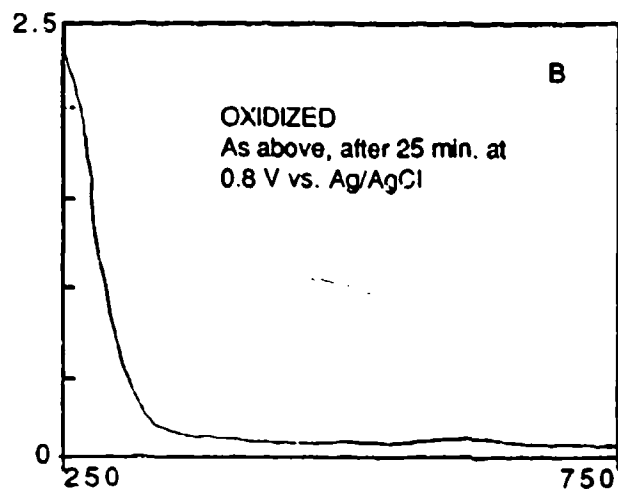
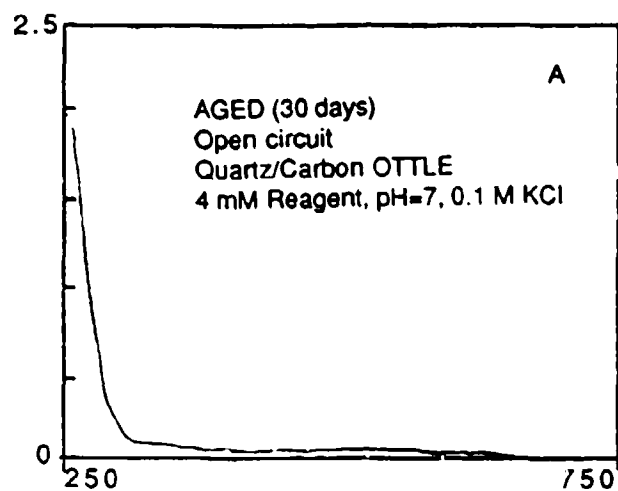


Figure 8b. Ligand vs. metal oxidation.
Case: ligand oxidized
Reagent 72, after 30 days

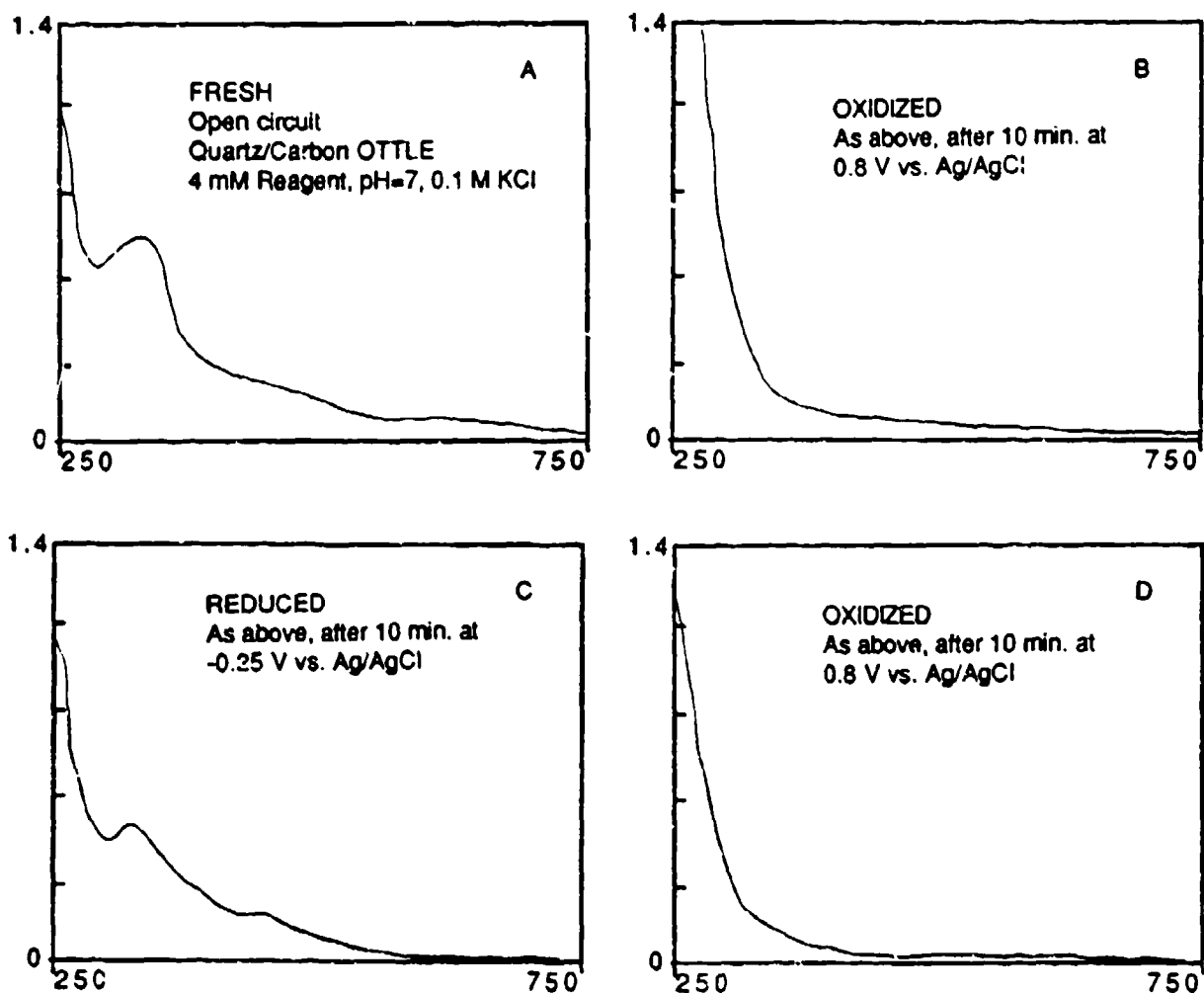


Figure 8c. Ligand vs. metal oxidation.
Case: metal oxidized
Reagent 192, fresh

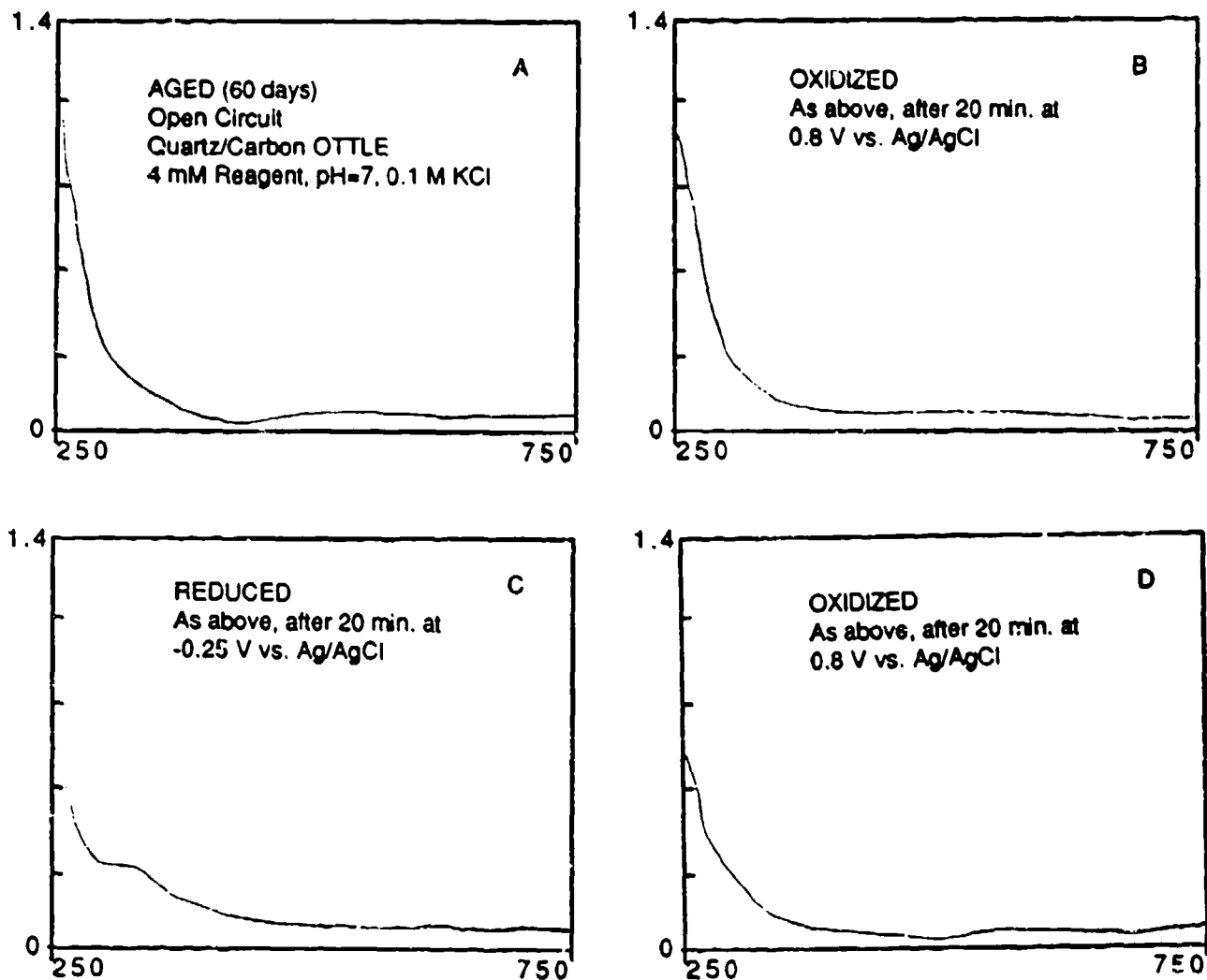


Figure 8d. Ligand vs. metal oxidation.
Case: metal oxidized
Reagent #192, after 60 days

Reagent #

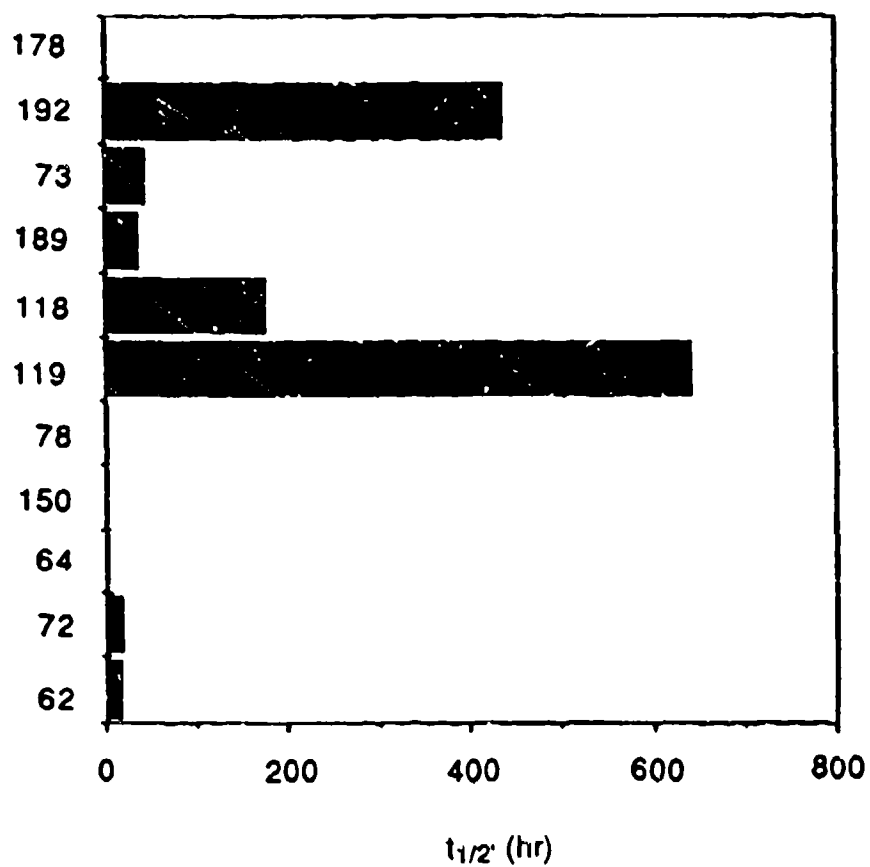


Figure 9. Variation of spectroscopic (static) lifetimes.

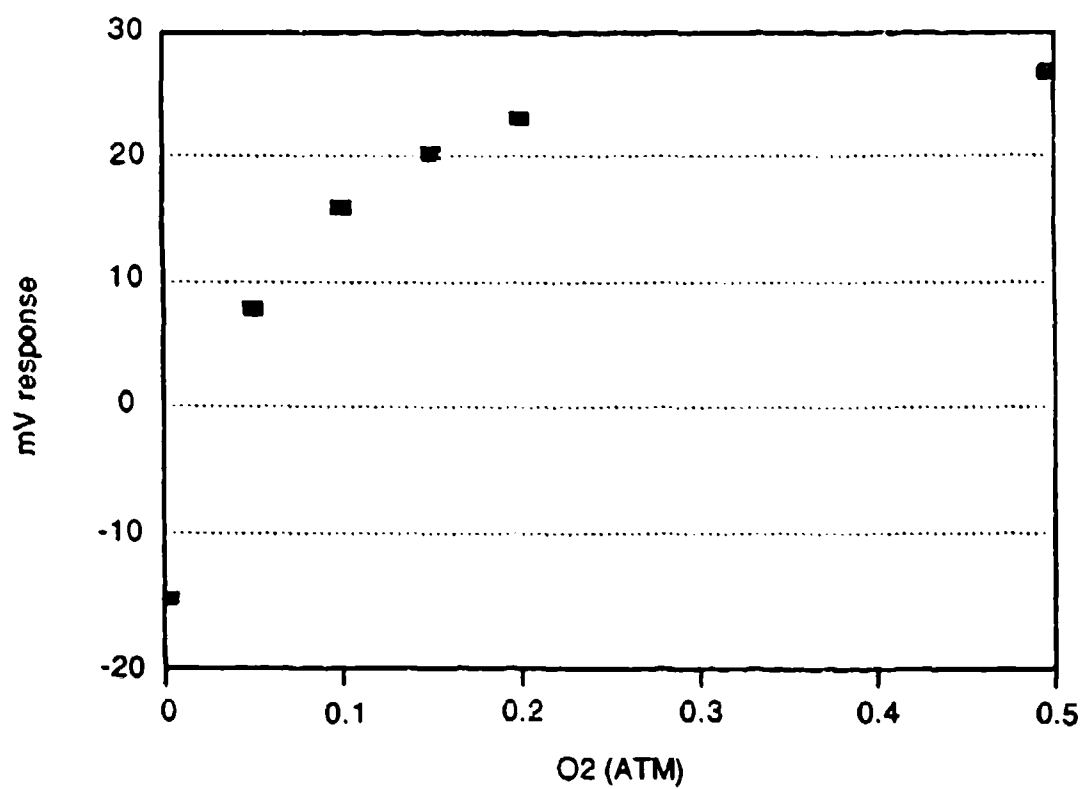


Figure 10. Calibration: thin solution film: Reagent #189.
Oxygen in nitrogen.

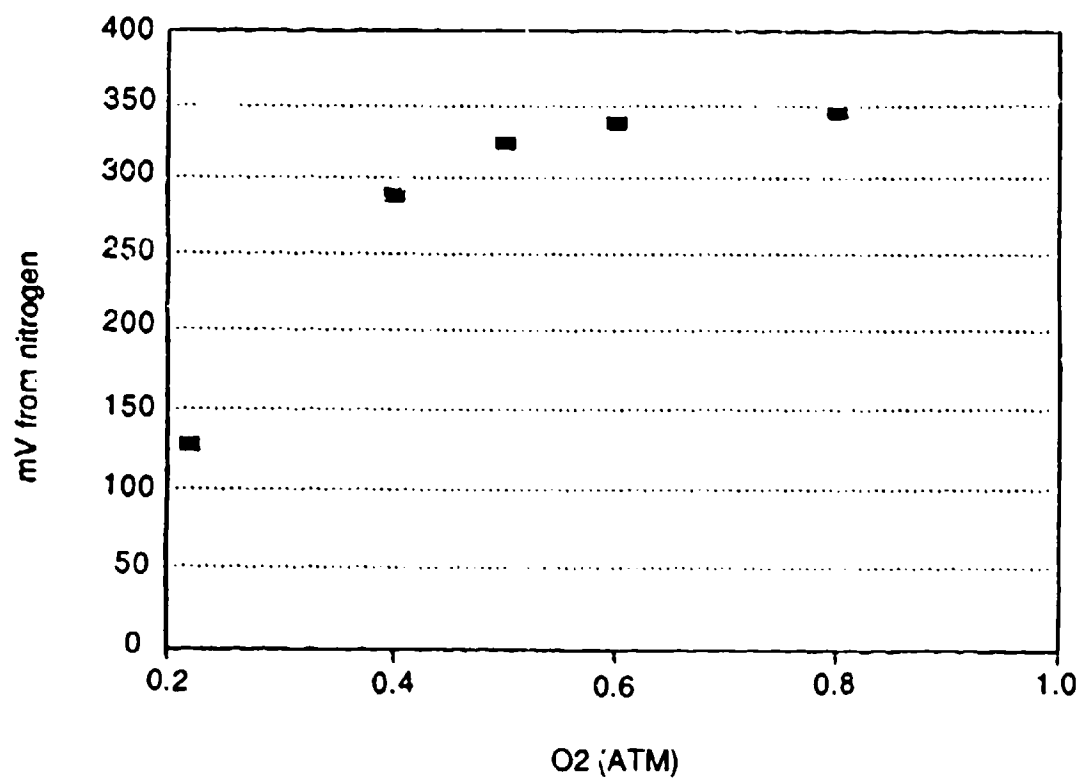


Figure 11. Solid polymer film: Reagent #189 in PVC.
Dissolved oxygen in water.

APPENDIX

ANALYSIS OF OXIDATION/REDUCTION PROBE DATA

The potential of a solution is given by the Nemst Equation when the reaction is written as a reduction.

$$E_{\text{cell}} = E^*_{\text{cell}} + \frac{RT}{nF} \ln \frac{[O]}{[R]}$$

where O and R refer to the oxidized and reduced forms, respectively.

Given that conditions exist such that a mixture of a ligand, L, and a metal, M, react completely to form the complex LM, then the potential of such of solution can be represented by Eq. A-2.



$$E_{\text{deoxy}} = E^*_{\text{deoxy}} + \frac{RT}{nF} \ln \frac{[\text{LM}^+]}{[\text{LM}]} \quad (\text{A-2})$$

When oxygen is introduced into the solution of LM, the oxygen complex LMO_2ML will form to an extent determined by the oxygen binding equilibrium constant. Thus, in this



solution the reactions defined by Eq. A-1 and A-3 will occur. The solution potential is then given by either Eq. A-4a or A-4b. The subscript oxy refers to the species concentration when oxygen is present.

$$E_{\text{oxy}} = E^*_{\text{oxy}} + \frac{RT}{nF} \ln \frac{[\text{LM}^+]^2[\text{O}_2]}{[\text{LMO}_2\text{ML}]} \quad (\text{A-4a})$$

$$E_{\text{oxy}} = E^*_{\text{deoxy}} + \frac{RT}{nF} \ln \frac{[\text{LM}^+]}{[\text{LM}]_{\text{oxy}}} \quad (\text{A-4b})$$

It is assumed that the initial concentration of the complex LM is C_i and that the concentration of oxidized complex LM^+ is always small under the present conditions. Then subtracting Eq. 4b from Eq. 2 and substituting yields after rearrangement Eq. 5a. Equation 5b allows the concentration of the unbound complex under oxygen to be calculated.

$$E_{\text{deoxy}} - E_{\text{oxy}} = \frac{RT}{nF} \ln \frac{[\text{LM}]_{\text{oxy}}}{[\text{LM}]} \quad (\text{A-5a})$$

$$\Delta E = E_{\text{deoxy}} - E_{\text{oxy}}$$

$$e^{\left(\frac{\Delta E nF}{RT}\right)} = \frac{[LM]_{oxy}}{C_1} \quad (A-5b)$$

The oxygen equilibrium constant can be calculated from Eq. A-6. Solving Eq. A-5b for $[LM]_{oxy}$ and substituting into Eq. A-6 relates the oxygen affinity to the oxidation/reduction potential data (Eq. A-7).

$$K_{O_2} = \frac{0.5(C_1 - [LM]_{oxy})}{[LM]_{oxy}^2 [O_2]} \quad (A-6)$$

where $[LMO_2ML] = 0.5(C_1 - [LM]_{oxy})$

$$K_{O_2} = \frac{0.5\left(C_1 - C_1 e^{\left(\frac{\Delta E nF}{RT}\right)}\right)}{\left(C_1 e^{\left(\frac{\Delta E nF}{RT}\right)}\right)^2 [O_2]} \quad (A-7)$$

Equation A-7 relates the voltages obtained through potentiometric means to the total oxygen affinity of the complex. However, for a sensor, one wants to relate oxygen concentration to a measured potential. As formulated above, the potential would actually consist of the measured potential with no oxygen around minus that when some oxygen is present.

Thus, Eq. A-7 can be reformulated to give $[O_2]$ in terms of the measured response and other constants of the system. Next rearrange Eq. A-7 to solve for $[O_2]$; factor C_1 and take the natural log of all terms. Equation A-8 gives the final form employed for relating the oxygen concentration to the potentiometric response (ΔE), reagent concentration (C_1), reagent oxygen affinity (K_{O_2}), and temperature (T).

$$\ln[O_2] = \ln \frac{0.5}{C_1 K_{O_2}} + \ln\left(1 - e^{\left(\frac{\Delta E nF}{RT}\right)}\right) - 2\frac{\Delta E nF}{RT} \quad (A-8)$$

Figure A-1 summarizes the theoretical response of a sensor for a constant reagent concentration and a range of different reagent oxygen affinities. Each line represents a reagent oxygen affinity.

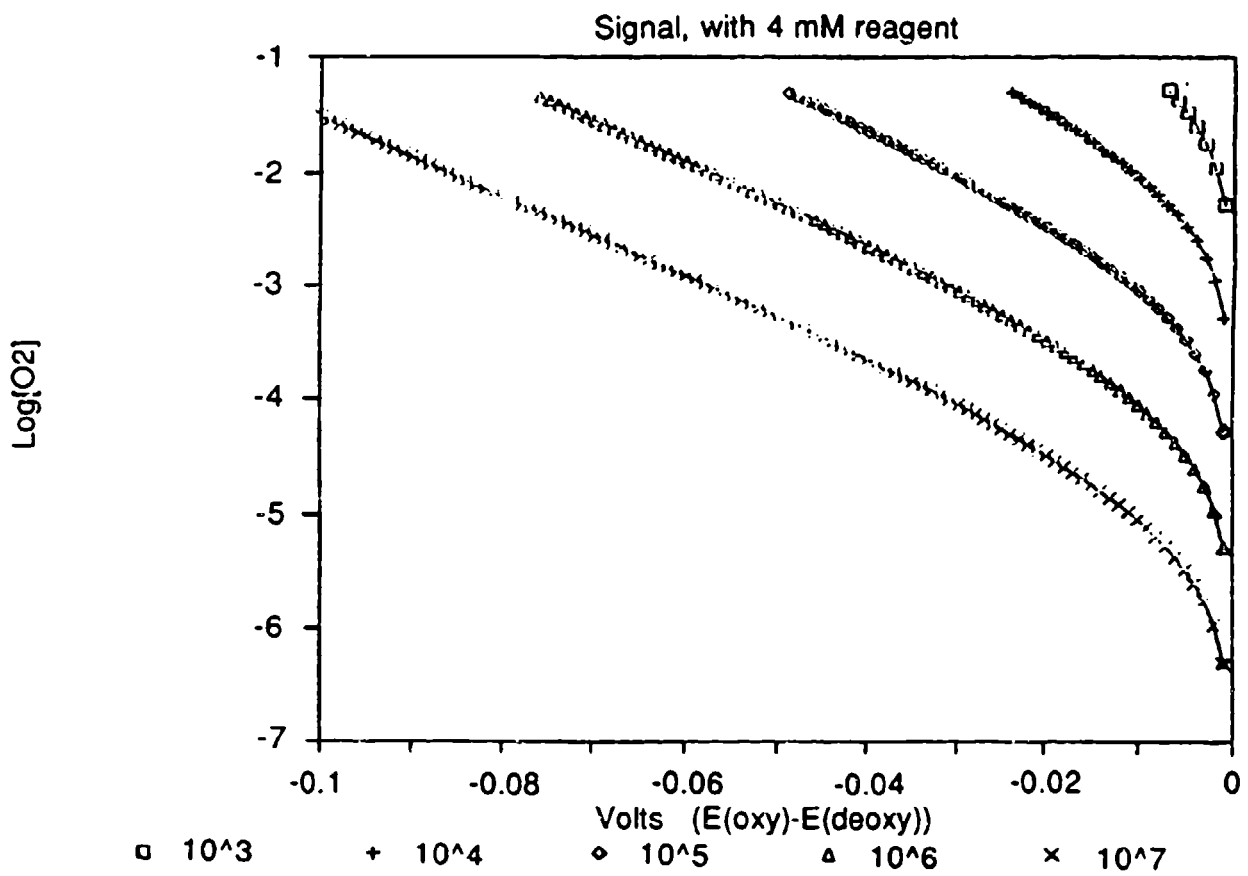


Figure A-1. Simulation of Potentiometric Sensor